

June 14, 1860.

General SABINE, R.A., Treasurer and Vice-President,
in the Chair.

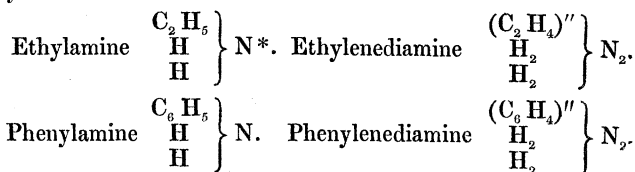
Francis Galton, Esq., Joseph Henry Gilbert, Esq., Thomas Hewitt Key, Esq., Joseph Lister, Esq., The Rev. Robert Main, Robert William Mylne, Esq., and Edward Smith, M.D., were admitted into the Society.

The following communications were read :—

- I. "Notes of Researches on the Poly-Ammonias."—No. VIII.
Action of Nitrous Acid upon Nitrophenylenediamine. By
A. W. HOFMANN, LL.D., F.R.S. Received April 5, 1860.

The experiments of Gottlieb have shown that dinitrophenylamine, when boiled with sulphide of ammonium, is converted into a remarkable base, crystallizing in crimson needles, generally known as nitrazophenylamine, and for which, in accordance with the views I entertain regarding its constitution, I now propose the name Nitrophenylenediamine. I owe to the kindness of Dr. Vincent Hall a considerable quantity of this substance, which is not quite easily procured.

I have made a few experiments with this compound in the hope of obtaining some insight into its molecular constitution. If, bearing in mind the numerous analogies between the radicals ethyl and phenyl, we assume that the latter, by the loss of hydrogen, may be converted into a diatomic molecule, phenylene C_6H_4 , corresponding to ethylene, the existence of a group of bases corresponding to the ethylene-bases cannot be doubted.



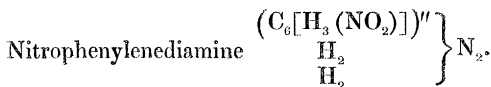
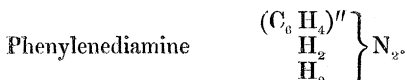
* H=1; O=16; C=12, &c.

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With the last-named body agrees in composition the compound known as semibenzidam, or azophenylamine, which Zinin obtained by exhausting the action of sulphide of ammonium on dinitrobenzol.

Those chemists, however, who have had an opportunity of becoming acquainted with the well-defined properties of ethylenediamine, will not be easily persuaded to consider the uncouth dinitrobenzol-product—sometimes appearing in brown flakes, sometimes as a yellow resin, rapidly turning green in contact with the air—as standing to smooth phenylamine in a relation similar to that which obtains between ethylenediamine and ethylamine; we much more readily admit a relation of this description between phenylamine and Gottlieb's crimson-coloured base, in which the clearly pronounced character of the former is still distinctly visible, although of necessity modified by the further substitution which has taken place in the radical.



Does the latter formula really represent the molecular constitution of the crimson needles? The degree of substitution of this body might have been determined by the frequently adopted process of ethylation. But even a simpler and a shorter method appeared to present itself in the beautiful mode of substituting nitrogen in the place of hydrogen, lately discovered by P. Griess. The red crystals undergo, indeed, the transformation, which he has already proved for so many derivatives of ammonia, with the greatest facility.

On passing a current of nitrous acid into a moderately concentrated solution of the nitrate of the base, the liquid becomes slightly warm, and deposits on cooling a considerable quantity of brilliant white needles, the purification of which presents no difficulty: spa-

ringly soluble in cold, readily soluble in boiling water, the new compound requires only to be once or twice recrystallized. Thus purified, this substance forms long prismatic crystals, frequently interlaced, white as long as they are in the solution, but assuming a slightly yellowish tint when dried, and especially when exposed to 100° : they are readily soluble both in alcohol and in ether. The new body exhibits a distinctly acid reaction; it dissolves on application of a gentle heat in potassa and in ammonia, without, however, neutralizing the alkaline character of these liquids; it also dissolves in the alkaline carbonates, but without expelling their carbonic acid. The new acid fuses at 211° C., and sublimes at a somewhat higher temperature, with partial decomposition. The sublimate consists of small prismatic crystals.

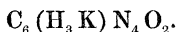
Analysis proves this substance to contain



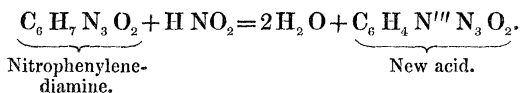
a formula which is confirmed by the analysis of a silver-compound,



and of a potassium-salt,

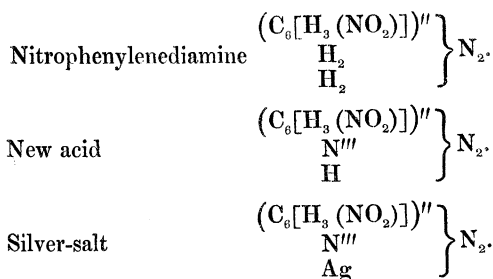


The analysis of the new compound shows that, under the influence of nitrous acid, nitrophenylenediamine exchanges three molecules of hydrogen for one molecule of nitrogen, three molecules of water being eliminated.



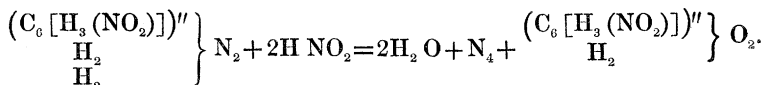
I do not propose a name for the new compound, which can claim but a passing interest, as throwing, by its formation, some light on the constitution of nitrophenylenediamine.

The composition of the new acid, and of its salts, shows that in the crimson-red base four hydrogen molecules are still capable of replacement; in other words, that this body contains four extra-radical molecules of hydrogen. The result of these experiments appears to confirm the view which, in the commencement of this Note, I have taken of the constitution of this body; at all events, the mutual relation of the several bodies is satisfactorily illustrated by the formulæ—



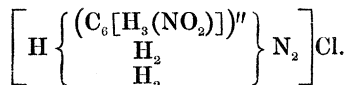
If the admissibility of this interpretation be confirmed by further experiments, the reaction discovered by Griess furnishes a new and valuable method of recognizing the degree of substitution in the derivatives of ammonia.

The new acid differs in many respects from the substances produced from other nitrogenous compounds. As a class, these substances are remarkable for the facility with which they are changed under the influence of acids, and more especially of bases. The new acid exhibits remarkable stability; it may be boiled with either potassa or hydrochloric acid without undergoing the slightest change. Even a current of nitrous acid passed into the aqueous or alcoholic solution is without the least effect. The latter experiment appeared of some interest; for if the action of nitrous acid, in a second phase of the process, had assumed the form so frequently observed by Piria and others, it might have led to the formation of the diatomic nitrophenylene-alcohol, according to the equation



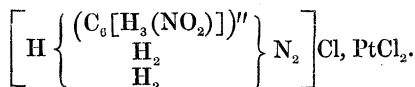
It deserves to be noticed that nitrophenylenediamine, although derived from two molecules of ammonia, is nevertheless a decidedly monacid base. Gottlieb's analyses of the chloride, nitrate, and sulphate left scarcely a doubt on this point. However, as some of the natural bases, quinine for instance, are capable of combining with either one or two molecules of acid, I thought it of sufficient interest to confirm Gottlieb's observations by some additional experiments. The crystals deposited on cooling from a solution of nitrophenylenediamine in concentrated hydrochloric acid, were washed with the same liquid and dried *in vacuo* over lime.

Analysis led to the formula



The dilute solution of this chloride is not precipitated by dichloride of platinum, nor can the double salt of the two chlorides be obtained by evaporating the mixed solutions, which, just as Gottlieb observed it, is readily decomposed with separation of metallic platinum. I had, however, no difficulty in preparing a platinum salt, crystallizing in splendid long brown-red prisms, by adding the dichloride of platinum to the *concentrated* solution of the hydrochlorate.

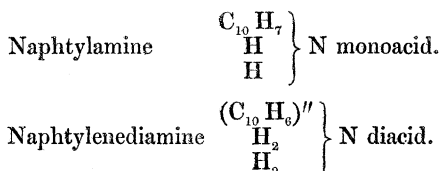
The platinum determination led to the formula



These experiments prove that, even under the most favourable circumstances, nitrophenylenediamine combines only with 1 equiv. of acid, while the ethylene-derivatives are decidedly diacid. The diminution of saturating power in nitrophenylenediamine, at the first glance, seems somewhat anomalous, but the anomaly disappears if the constitution of the body be more accurately examined. It cannot be doubted that the diminution of the saturating power is due to the substitution which has taken place in the radical of the diamine. I have pointed out at an earlier period*, that the basic character of phenylamine is considerably modified by successive changes introduced into the phenyl-radical by substitution. Chlorphenylamine, though less basic than the normal compound, still forms well-defined salts with the acids; the salts of dichlorphenylamine, on the other hand, are so feeble, that, under the influence of boiling water, they are split into their constituents; in trichlorphenylamine, lastly, all basic characters have entirely disappeared. Again, on examining the nitro-substitutes of phenylamine, we find that even nitrophenylamine is an exceedingly weak base, whilst dinitrophenylamine is perfectly indifferent. What wonder, then, that a molecular system, to which in the normal condition we attribute a diacid character, should, by the insertion of special radicals, be reduced to monoacidity? The normal phenylenediamine, which remains to be discovered, will doubt-

* Mem. of Chem. Soc. vol. ii. p. 298.

less be found to be diacid, like the diamines derived from ethylene. Even now the group of diacid diamines is represented in the naphthyl-series :



The body which I designate by the term Naphthylenediamine, is the base which Zinin obtained by the final action of sulphide of ammonium upon dinitronaphthaline. This substance, originally designated seminaphthalidam, and subsequently described as naphthalidine, combines, according to Zinin's experiments, with 2 equivalents of hydrochloric acid*.

II. "On the Formula investigated by Dr. BRINKLEY for the general Term in the Development of LAGRANGE'S Expression for the Summation of Series and for successive Integration." By Sir J. F. W. HERSCHEL, Bart., F.R.S. &c. Received April 26, 1860.

(Abstract.)

In the Philosophical Transactions for the year 1807, Dr. Brinkley has investigated an expression of the general term of the series of Lagrange and Laplace for the finite differences and integrals of any function u in terms of its differential coefficients and common integrals of successive orders *ad infinitum*, which is in effect equivalent to the development of the functions $(e^t - 1)^n$ and $(e^t - 1)^{-n}$ in powers of t . The demonstration of the formulæ arrived at, as there stated, is circuitous and extremely difficult to follow; so much so as to render a simpler and easier one a desideratum in analysis, as there are probably few who have had the patience to follow it out to its conclusion.

More recently (Philosophical Transactions, 1816), the author of the present paper arrived at a general and extremely simple expression

* Liebig's Annalen, vol. lxxxv. p. 328.